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THE WIEDEMANN-FRANZ LAW IN SEMICONDUCTOR AND METAL GLASSES

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In the present paper relations for the Wiedemann-Franz law in amorphous semiconductors and metals are derived on the basis of the theory of the modified relaxation time. Measurements have shown that the Lorentz number is often a significant function of temperature. The calculation of the electronic component of the thermal conductivity from the electrical conductivity under the assumption that the Lorentz number is constant (as it is often used) can lead to considerable errors. Because of the absence of suitable semiconductor glasses the results following from our theory were verified only indirectly (by means of the Seebeck coefficient) and in metal glasses by direct measurement, respectively. The agreement between the measured and the calculated curves of the temperature dependences of the Lorentz number can be considered as good.

ЗАКОН ВИДЕМАНА-ФРАНЦА ДЛЯ ПОЛУПРОВОДНИКОВ И МЕТАЛЛИЧЕСКИХ СТЁКОЛ

В данной работе получена зависимость типа закона Видемана-Франца для аморфных полупроводников и металлов, исходя из теории модифицированной релаксации. Измерения показали, что число Лоренца часто является существенной функцией температуры. Вычисление электронной составляющей теплопроводности из электропроводности в случае предположения, что число Лоренца является константой (как это часто делается), приводит к заметным ошибкам. Вследствие отсутствия подходящих полупроводниковых стёкол результаты, вытекающие из предложенной теории, были проверены только косвенным образом (с помощью коэффициента Зеебека), а в металлических стёклах с помощью прямых исмерений. Согласие между измеренными и вычисленными кривыми температурной зависимости числа Лоренца можно считать хорошим.

I. INTRODUCTION

In recent works the study of semiconductor and metal glasses has been oriented towards optical properties and electrical conductivity, less towards thermoelectric properties and magnetoresistivity and only seldom towards thermal properties. For studies of the lattice thermal conductivity, the electronic component is usually subtracted from the total thermal conductivity using a formal application of the Wiedemann-Franz law (which is expressed in the form for crystalline materials) to non-crystalline semiconductors as well as to metals [1]. There are not enough reasonable arguments for such a procedure because it is widely known that the transport parameters have in principle different expression in the non-crystalline phase than in the crystalline one.

The existing theories of non-crystalline materials do not give any full solution of this problem, because all of the succesful theories of electrical conductivity (the theory of hopping conductivity [2, 3], the percolation theory [4, 5], the theories based on the Frenkel-Poole mechanism [6, 7] etc.) cannot be practically applied to the electronic thermal conductivity and the more generally formulated theories [8] do not give results suitable for experimental verification. The possibility of solving this problem arose, when the concept of the modified relaxation time was formulated by the method of the Boltzmann formalism [9, 10]. The results obtained by this theory are in a good agreement with the thermal dependences of transport parameters in semiconductor glasses. It is also very effective for the explanation of the peculiarity of the temperature dependences of the electrical conductivity in metal glasses.

We presume that this theory will give reliable information about the relation between the electrical conductivity and the electronic thermal conductivity of these materials, i.e. about the Lorentz number and its dependences on the temperature.

II. FUNDAMENTAL IDEAS

The ratio of the electronic component of the thermal conductivity, i.e. the Wiedemann-Franz law in the Boltzmann formalism is expressed by relation [12].

$$\frac{\lambda}{\sigma}=\frac{1}{e^2T}\,\frac{\langle\tau\rangle\langle\tau E^2\rangle-\langle\tau E\rangle^2}{\langle\tau\rangle^2}, \tag{1}$$

where the quantity $\langle\tau E^n\rangle$ is defined by the function

$$\langle\tau E^n\rangle=\frac{4}{3\sqrt{\pi}(kT)^{5/2}}\int_0^\infty E^{n+3/2}\tau(E)\exp\left(-E/kT\right)\mathrm{d}E \tag{2}$$

for the classical statistics and by the function

$$\langle\tau E^n\rangle=E_F^{-3/2}\int_0^\infty e^{n+3/2}\tau(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E, \tag{3}$$

for the Fermi-Dirac statistics. In these relations E is the energy of the charge carriers, $\tau(E)$ the relaxation time, k the Boltzmann constant, T the temperature, E_F the Fermi level and f_0 the equilibrium Fermi-Dirac function

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$$f_0(E)=\frac{1}{\exp\left[-\frac{E_F-E}{kT}\right]+1}. \tag{4}$$

The Lorentz number is defined by the coefficient in the relation $\lambda/\sigma=LT$.

According to papers [9, 10] the relaxation time of non-crystalline materials can be expressed with the aid of the relaxation time $\tau_k(E)$ characterizing the crystal by the formula

$$\frac{1}{\tau(E)}=\frac{1}{\tau_k(E)}\left\{1+\frac{l_k}{d}\frac{1-P(E)}{P(E)}\right\}=\frac{1}{g(E)\tau_k(E)}, \tag{5}$$

where d is the mean distance between the local potential barriers (connected with the vanishing of the long range order valid for a crystal, l_k the free path of the charge carriers corresponding to the crystalline state and $P(E)$ the probability of tunnelling the charge carriers through the barriers defined (in the simple case of a square-type barrier with the hight W and width d_b) by the relation

$$P(E)\approx\exp\left\{-\frac{4\pi}{h}[2m^*(W-E)]^{1/2}d_b\right\}=\exp[-\beta(W-E)^{1/2}]. \tag{6}$$

Here m^* is the effective mass of the charge carriers, h the Planck constant and $\beta=4\pi d_b(2m^*)^{1/2}/h$.

With regard to the mentioned facts it is necessary to divide the region of integration in the integrals (2) and (3) into the regions:

a) the region $0<E<W$, in which $\tau(E)=\tau_k(E)g(E)$

b) the region $W<E<\infty$, in which $\tau(E)=\tau_k(E)$.

Then, e.g., the integral (2) can be divided into two components as follows

$$\langle\tau E^n\rangle=\frac{4}{3\sqrt{\pi}(kT)^{3/2}}\left\{\int_0^W E^{n+3/2}\tau_k(E)g(E)\exp[-E/kT]\,\mathrm{d}E+\right. \tag{7}$$

$$\left.+\int_W^\infty E^{n+3/2}\tau_k(E)\exp[-E/kT]\,\mathrm{d}E.\right.$$

Both parts of this expression have a clear physical meaning: the first of them corresponds to the contribution of the electrons with an energy smaller than the height of the potential barriers, the second to the contribution of the electrons moving above the barriers.

It is impossible to find the analytical solution of the mentioned integrals with regard to the functions $\tau(E)$, $P(E)$ and $f_0(E)$, therefore we can give the calculation only for special cases. For non-crystalline semiconductors in which we use classical statistics (i.e. integral (2)), due to the low concentration of charge carriers we divide the whole interval of temperature into three regions:

a) Very low temperatures defined by the condition $E\ll W$. In this case $P(E)\ll 1$ and

$$\tau_1(E)\approx\tau_k(E)\frac{d}{l_k}P(E). \tag{8}$$

Under this condition the second integral in the relation (7) can be neglected in comparison with the first integral.

b) Mean temperatures, in which $P(E)<1$; for the sake of mathematical simplicity we shall use the function (5) in the form

$$\tau(E)\approx\tau_1(E)\left\{1+\frac{l_k-d}{d}\exp[-\alpha(W-E)]\right\}. \tag{9}$$

The characteristic constant α is defined by the approximative relation $\alpha\approx\approx l_k^2\beta^2/2d$.

c) High temperature defined by the condition $E\gg W$. The first integral in the relation for this case can be completely omitted.

It is necessary to use the Fermi-Dirac statistics in non-crystalline metals. The mathematical simplicity (9) is not useful, because the function $f_0(E)$ is not analytically integrable. We shall therefore try in this case to approximate for the calculation of these integrals the Fermi-Dirac function by a simpler function.

III. THE LORENTZ NUMBER IN SEMICONDUCTOR GLASSES

The relaxation time of the crystalline semiconductors $\tau_k(E)$ is usually expressed in the form

$$\tau_k(E)=\tau_0E^s, \tag{10}$$

where s is a characteristic exponent of the scattering processes in the crystal ($s=-1/2$ for thermal scattering and $s=3/2$ for scattering on charged defects). Under the conditions mentioned above the following relations can be obtained for the Lorentz number:

$$L_1(T)=(5/2+s)(k/e)^2\,1/(1-bT)^2, \tag{11}$$

where $b=\beta k/2\sqrt{W}$.

For the last two regions we shall assume that the exponent s has the value $s=-1/2$. In these cases the following approximate relations were found:

$$L_2(T)=(k/e)^2(W_1/kT)^2\exp[2W_1/kT], \tag{12}$$

$$L_3(T)=(k/e)^2\left\{\frac{1+4(kT/W)+2(kT/W)^2}{(1+kT/W)^2}\right\}, \tag{13}$$

where the parameter W_1 is defined by the equation

$$\frac{1}{W_1}=\frac{\beta}{2\sqrt{W}}+\alpha. \tag{14}$$

The expressions (11—13) give information about the temperature dependences of the Lorentz number. For $T\to\infty$ there is $L_1=(5/2+s)(k/e)^2=L_k$, which corresponds to the expression of the Lorentz number for the crystalline state. Its value increases with increasing temperature and at $bT=1$ we have $L\to\infty$.

This singularity really does not exist and is only the result of our approximations. However, the increase of the Lorentz number with temperature in this region can be the real effect as it will be seen later. For the usual values typical for the chalcogenide amorphous semiconductors [13] $\{\beta=4\pi d_b(2m^*)^{1/2}/h\approx 4\times10^{10}$ and $b\approx 3\times10^{-3}\}$, the critical temperature $T_k\sim 1/b$ is at room temperatures. Comparing with the optical measurements [14] we can state that for these semiconductors the value of W_1 is of the order 0.1 eV. According to relation (12), the Lorentz number has the values $L>L(T=0)$, but decreases with temperature, while at high temperatures ($W\simeq 0.2$ eV is already $kT(W\ll 1)$) the Lorentz number has the minimum value and is practically independent of temperature. The temperature dependence $L=L(T)$ is in Fig. 1. In the experimental part we shall show that this type of the Lorentz number temperature dependence is very probable.

IV. THE METAL GLASSES

In the metal glasses as in the crystalline metals there is a high concentration of charge carriers. In this case we have to use the Fermi-Dirac statistics for the solution of transport phenomena. As in equation (7) we can express the mean value of the term $\langle\tau E^n\rangle$ with two integrals

$$\langle\tau E^n\rangle=E_F^{-3/2}\int_0^\infty \tau_k(E)E^{n+3/2}\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E\times \tag{15}$$
$$\times\left\{1-\frac{\int_0^W[1-g(E)]E^{n+3/2}\tau_k(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E}{\int_0^\infty E^{n+3/2}\tau_k(E)\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E}\right\}.$$

The integrals in the interval $\langle 0,\infty\rangle$ can be transformed into the Fermi integrals using the transformation

$$\int_0^\infty E^{n+3/2}\left(-\frac{\partial f_0}{\partial E}\right)\mathrm{d}E=(n+3/2)(kT)^{n+3/2}\Gamma(n+1)F_{n+1/2}(\eta), \tag{16}$$

where $F_{n+1/2}(\eta)=[1/\Gamma(n+1)]\int_0^\infty x^n/\exp[x-\eta]\,\mathrm{d}x$ are tabulated. The remaining integrals can be calculated only numerically. For the more general conclusions it is more advantageous to obtain an approximative analytical solution. For this purpose we used as in [11] the approximations:

$$1-g(E)=1-\exp[-\beta(W-E)^{1/2}]\approx 1-(E/W)^p, \tag{17}$$

$$f_0(E)=\frac{1}{\exp\left[-\dfrac{E_F-E}{kT}\right]+1}\approx 1-\frac{1}{2}\left(\frac{E}{E_F}\right)^q. \tag{18}$$

We shall see that the influence of the approximation (17) is not too important, as it concerns only the electrons with the energy $E\ll W$. The second approximation is valuable only for $E<E_F$, which is sufficient because of the always valid inequality $W<E_F$. The exponent q can be specified from the equality of the derivatives of both functions for $E=E_F$. We obtain the result

$$q=E_F/2kT. \tag{19}$$

To what extent this approximation is satisfying is shown in Fig. 2, where both functions are calculated for $E_F=1$ eV and the temperature $T=100$ K, 300 K and 500 K.

With regard to these approximations the Wiedermann-Franz law (1) can be expressed for metal glasses by the relation ($s=-1/2$).

$$\frac{\lambda}{\sigma}=\left(\frac{k}{e}\right)^2T\frac{1}{F_0^2[1-G(T)]^2}\left\{A_0-A_1\left(\frac{W}{kT}\right)+A_2\left(\frac{W}{kT}\right)^2-\right. \tag{20}$$
$$\left.-A_3\left(\frac{W}{kT}\right)^3+A_4\left(\frac{W}{kT}\right)^4,\right.$$

where

$$A_0=6F_0F_2-4F_1^2,\quad A_1=3\left(\frac{W}{E_F}\right)^qF_2\frac{pq}{(p+q+1)(q+1)},$$

$$A_2=2\left(\frac{W}{E_F}\right)^qF_1\frac{pq}{(p+q+2)(q+2)},\quad A_3=\frac{1}{2}\left(\frac{W}{E_F}\right)^qF_0\frac{pq}{(p+q+3)(q+3)},$$

$$A_4=\frac{1}{4}\left(\frac{W}{E_F}\right)^{2q}\left\{\frac{(pq)^2}{(p+q+1)(q+1)(p+q+3)(q+3)}-\frac{(pq)^2}{(p+q+2)^2(q+2)^2},\right.$$

$$G(T)=\frac{1}{2F_0}\left(\frac{W}{E_F}\right)^q\frac{W}{kT}\frac{pq}{(p+q+1)(q+1)}.$$

If the Fermi level is high above the value $W(E_F\gg W)$, the coefficients $A_1=A_2=A_3=A_4=0$ and $G(T)\to 0$. In this case, we can write relation (20) in the form

$$\frac{\lambda}{\sigma}=\left(\frac{k}{e}\right)^2T\frac{6F_0F_2-4F_1^2}{F_0^2}, \tag{21}$$

which corresponds to the expression of the Wiedemann-Franz law in crystalline metals. In this case almost no change may appear during the amorphization of the metals. However, when $E_F \approx W$, i.e. the Fermi level descends close to the level of defects, it is necessary to consider also the other term. In this case, however, the individual coefficients are only slightly dependent on temperature and we can consider them as constants. As always $G(T)<1$, we need not consider this dependence on temperature. Under this condition the Wiedemann-Franz law can be expressed in the form

$$\frac{\lambda}{\sigma}=B_0T-B_1+B_2\frac{1}{T}-B_3\frac{1}{T^2}+B_4\frac{1}{T^3}, \tag{22}$$

and the temperature dependence of the Lorentz number is determined by the relation

$$L=B_0-B_1\frac{1}{T}+B_2\frac{1}{T^2}-B_3\frac{1}{T^3}+B_4\frac{1}{T^4}. \tag{23}$$

The dependences expressed in this form can be used for comparison with the experiment.

V. DISCUSSION

The experimental verification of the validity of the Wiedermann-Franz law is difficult because of obtaining the whole thermal conductivity immediate by measurement, i.e. the sum of the lattice and the electronic component. Because the lattice thermal conductivity lies within the order of magnitude of a 10^{-1} Wm^{-1}K^{-1} in the materials under the condition

$$\sigma>2\times10^4\ \Omega^{-1}\text{m}^{-1}, \tag{24}$$

the electronic component of the thermal conductivity predominates. In these materials the term $\lambda/\sigma T$ defines directly the Lorentz number. All the amorphous semiconductors prepared up to now are below this value, therefore the Wiedemann-Franz law cannot be verified by direct measurement. At present the attention is centred upon the so called "narrow gap" amorphous semiconductors (Bi_2Te_3, Sb_2Te_3, etc.), in which the electronic conductivity could reach the above mentioned value. Meanwhile we can draw a conclusion, as regards the curves of the dependence λ/σ, only indirectly. From this aspect it is remarkable that those transport parameters of noncrystalline semiconductors, which contain in their expression only the integrals of the type $\langle\tau\rangle$, $\langle\tau^2\rangle$, etc. (e.g. electrical conductivity, Hall mobility, magnetoresistivity) have no extremes in the temperature dependence. However, the Seebeck coefficient, e.g., which contains the integral for the type $\langle\tau E\rangle$ has an extreme very similar to the dependence shown in Fig. 1 [15, 16]. As the relation of the Lorentz number contains the expression of the type $\langle\tau E\rangle$, we can assume that the dependence in Fig. 1 is real.

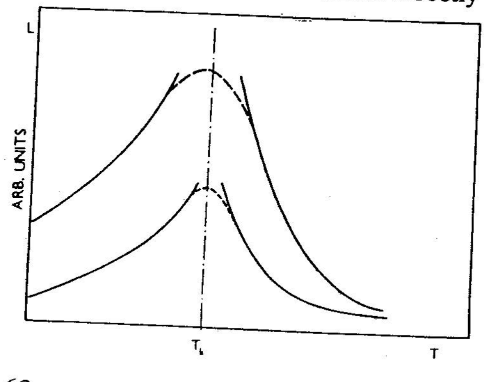

Fig. 1. Temperature dependence of the Lorentz number according to approximative relations (11), (12) and (13).

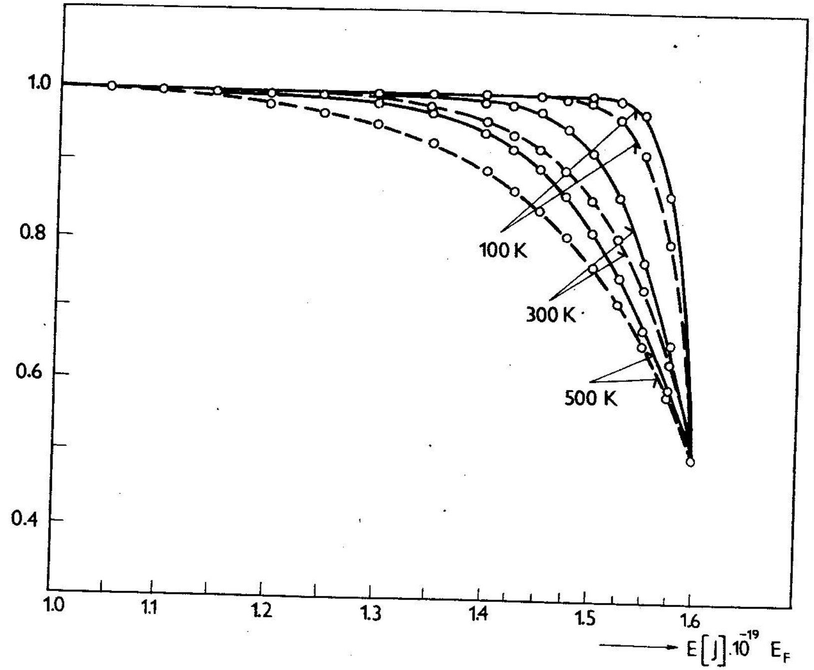

Fig. 2. Calculated dependences of the Fermi-Dirac function on the energy for the following values of temperature: $T=100$ K, 300 K, 500 K, according to relation (4) (continuous line) and approximative relation (18) (dashed line).

In the metal glasses, except for the range of very low temperatures, the condition $\lambda_e>\lambda_m$ is always valid and therefore the Wiedemann-Franz law can be verified by direct measurements. However, definite data for this region are not given, measurements were made on samples of $Pd_{80}Si_{20}$ [17]. The temperature dependence of the measurements of electrical conductivity of this metal glass is shown in Fig. 3, the ratio λ/σ in Fig. 4 and the Lorentz number in Fig. 5. The curves in Figs. 4 and 5 have been found by the Kohlrausch method [18]. Even if the measurements have been characterized by a considerable error, we can assume that the measured dependence agrees with reality. Up to about 650 K the sample remained in the amorphous state (it can contain only the nuclei of the crystalline phase) and above this temperature the sample crystallized, as shown by a sudden break in the measured dependences.

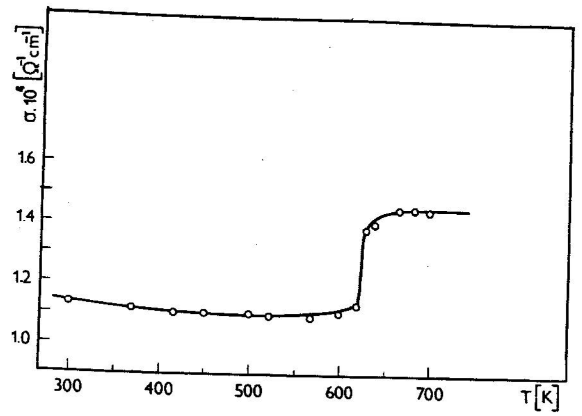

Fig. 3. Measured temperature dependence of the electrical conductivity for the samples of $Pd_{80}Si_{20}$.

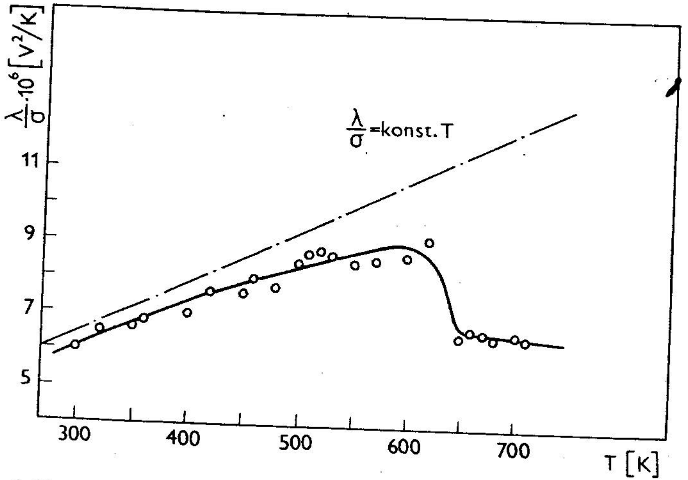

Fig. 4. Measured temperature dependence of the ratio λ/σ for samples of $Pd_{80}Si_{20}$.

It is clear that the dependence in Fig. 4 cannot be considered to be a stright line, which corresponds to the dependence $\lambda/\sigma = \text{const.}\ T$ characteristic for the crystal. Let us consider that the exponents p and q have large values. For $E_F \approx 1$ eV and $T = 300$ K is $q = E_f/2kT \approx 19$ and for $E \to E_F$ $p \to \infty$. Therefore the coefficient A_4 has a value near zero and if we omit also the term with the coefficient A_3, which is less important for the higher temperatures we obtain from relation (22), the function

$$\frac{\lambda}{\sigma} = B_0 T - B_1 + B_2 \frac{1}{T}. \qquad (25)$$

This function (continuous line in Fig. 4) approximates the measured dependence very well. Analogically for the Lorentz number we get the function

$$L = B_0 - B_1 \frac{1}{T} + B_2 \frac{1}{T^2}. \qquad (26)$$

This function has the extreme for the temperature $T_k = 2B_2/B_1$ and the measured dependence (Fig. 5) can be considered as the part following its maximum.

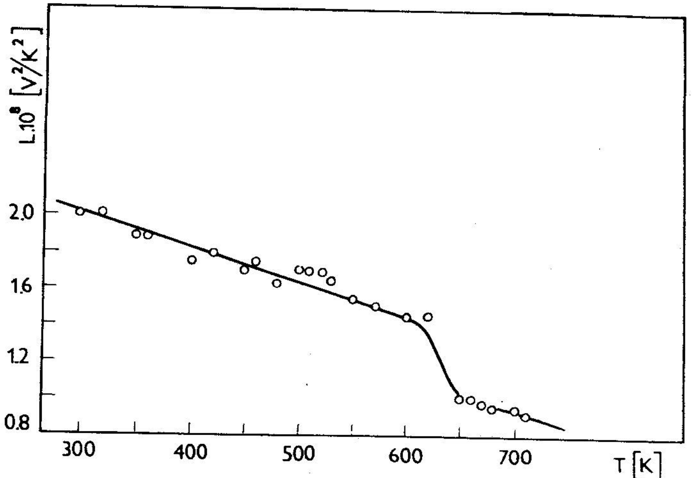

Fig. 5. Temperature dependence of the Lorentz number for samples of $Pd_{80}Si_{20}$.

VI. CONCLUSION

In the present paper it has been shown that the Lorentz number is generally the function of temperature in non-crystalline metals and semiconductors. This conclusion has been verified also experimentally on metal glasses and indirectly on semiconductor glasses. Deviations from the supposed constant value are relatively large and they can reach values>100%; therefore we must be careful in the application of the Wiedemann-Franz law valid for crystals with the temperature independent Lorentz number in the case of the non-crystalline solid state.1)

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1) Note at the proofs: Recent investigations have shown that in some amorphous metals the condition $E_F < W$ can be also fulfilled. Because of very small differences $(W - E_F)$ our results remain correct in this case.